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OFFICE OF PREVENTION, PESTICIDES AND TOXIC SUBSTANCES

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MEMORANDUM

SUBJECT: Environmental Fate and Ecological Risk Assessment for Mancozeb, Section 4

Reregistration for Control of Fungal Diseases on Numerous Crops, a Forestry

Use on Douglas Firs, Ornamental Plantings, and Turf.

TO:

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FROM:

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The EFED screening level Environmental Risk Assessment is attached. This RED document should be considered with the document for ETU, the degradate of concern for mancozeb.

In this document three important abbreviations are used: Parent mancozeb, Mancozeb residue and **Bound species.** Parent mancozeb is the polymeric mancozeb parent present in the active ingredient. Mancozeb Residue are suites of multi species residues resulting from degradation of the polymeric mancozeb parent. The suite includes the following: (a) species reported to be present but not specifically identified: variable/low molecular weight polymeric chains (i.e polymer fragments), monomeric species, and EBDC ligand in association with other metal ions that might be present in the environment; (b) species identified and quantified: Transient species, ETU and ETU degradates; and (c) un-identified species that bound to soil and sediment particles (referred to as **Bound species**).

The following is an overview of our findings:



Risk Summary

There are chronic risks to birds and mammals. The chronic exceedances to birds range from a high RQ of 1,138 on turf to a low of 2 on citrus. For mammals, the range of RQ exceedance is from a high of 94 on turf to a low of 1 on peanuts. There are acute and chronic risks to freshwater fish and invertebrates; and acute risks to estuarine/marine fish and invertebrates. The acute RQs exceeding freshwater fish endangered species LOCs for mancozeb's uses range from 0.05 to 0.39. The chronic RQs exceeding LOCs for freshwater fish range from 1.46 to 2.83. The acute freshwater invertebrates' RQs exceeding endangered species LOCs range from 0.07 to 0.31 with chronic RQs ranging from 1.07 to 1.97. The acute estuarine/marine fish RQs exceed endangered species LOCs ranging from 0.05 to 0.11. Estuarine/marine invertebrate acute RQs exceed LOCs ranging from 2.31 EFED does not calculate risk quotients to conduct risk assessments on terrestrial invertebrates. Based on the lack of acute mancozeb toxicity to honeybees, EFED expects a low acute risk to nontarget terrestrial insects. Due to lack of data EFED did not assess risks to terrestrial plants or fully assess risks to aquatic plants. Based data for one surrogate species, mancozeb's use patterns exceed acute risk LOCs for nonvascular aquatic plants with acute RQs ranging from 1.19 to 3.78. EFED did not assess chronic risks to estuarine/marine fish and invertebrates due to lack of data.

Risk to the Water Resources

Mancozeb is non-persistent as it is expected to decompose rapidly (reach <10% of the applied within 3 days) by hydrolytic reactions in the main compartments of the natural environment. The terminal degradate of concern in the process of mancozeb decomposition is ETU, a B2 carcinogen. Therefore, risk assessment for the water resource from the common EBDCs degradate ETU, was performed for the application of all EBDCs including mancozeb. The reader is referred to the accompanied ETU document for this assessment.

Uncertainties

(1) Environmental Fate

EECs for *mancozeb parent* were estimated for water bodies using hydrolysis half-lives. The same water hydrolysis half-lives were used for soils assuming sufficient moisture is available in soil pores for hydrolysis to occur at the same rate. Uncertainty exists on whether half-lives used are applicable because of two reasons. The *first* reason is related to whether *mancozeb parent* applied into the environment is similar to that used in hydrolysis studies. No data was presented on the physical nature of the parent used in these studies compared to that present in technical active ingredient or end use products manufactured/formulated by various companies. The *second* reason is that soil moisture level is expected to impact resultant EECs. Lower EECs are expected in irrigated and/or rain-fed soils with high water holding capacity (WHC) and higher EECs are expected in low WHC soils under dry conditions. Giving the fact that mancozeb is applied to growing crops, moisture is expected to be available for parent to hydrolyze at rate near or just below that determined from aqueous hydrolysis half-lives.

EECs for *mancozeb residue* were estimated using the physicochemical properties and hydrolysis half-lives of *parent mancozeb* in addition to aerobic soil metabolism half-lives and sorption coefficients which were assigned to this residue rather than the parent. In all aerobic soil studies two separate sets of determinations were conducted: the *first* was to obtain data for calculating half-lives using the CS_2 -method to quantify the parent while the *second* was to characterize the bio-degradation process. EFED believes that half-lives calculated from the *first* set of determinations represent

hydrolytic decomposition of *mancozeb parent* rather than bio-degradation. Rapid degradation of *mancozeb parent* produces a residue, the *mancozeb residue*, which appears to be affected by slow degradation as indicated by production of CO₂. Part of this residue may contain precursor(s) for the degradate of concern, ETU. Therefore, EFED used the *second* set of experiments/determinations (radioactivity data) for calculating half-lives and assigned it to the *mancozeb residue*. Uncertainty exists in these residue half-lives as they are affected by the validity of the assumption that the only bio-degradation of the residue was represented by evolved CO₂. Data obtained on degradates were not used as it were affected by impurities in the test materials, hydrolytic reactions and possible artificial degradation during extraction.

In this RED, aerobic soil half-lives calculated from the CS_2 -method are considered to represent hydrolysis of *mancozeb parent* into its residue as modified by soil conditions (i.e. moisture content, pH and O_2 concentration). In contrast, half-lives calculated from evolved CO_2 are considered to represent bio-degradation of *mancozeb residue* left in the soil which appears to occur in parallel with hydrolytic decomposition of the parent. Likewise, calculated adsorption/desorption characteristics (K_d and K_{oc}) are thought to represent *mancozeb residue* as it were approximated from column leaching studies; with no 1/n value to indicate the degree of non-linearity for the Freundlich constant.

In the degradation process for mancozeb Mn and Zn ions/salts are expected to dissipate into the environment. No data were presented to evaluate the risk that might be associated with this release and therefore, uncertainty exists in this aspect of risk assessment.

(2) Ecological Effects

EFED is uncertain about mancozeb's acute risk to nontarget terrestrial plants and needs testing performed at mancozeb's maximum rate of application in the environment. EFED has not received studies to evaluate the acute risk of *mancozeb residues* to vascular aquatic plants and is uncertain about this risk. EFED has received one acute study for 1 of 4 surrogate species needed to evaluate the acute risk to nonvascular aquatic plants. This one study when compared to *mancozeb residues*' exposure showed the acute RQs exceeded LOCs. EFED needs testing performed on 3 more surrogate species to evaluate fully the acute risk to nonvascular aquatic plants. EFED has no data to evaluate the chronic effects to estuarine/marine organisms and is uncertain about the chronic risks to estuarine/marine organisms. EFED needs whole sediment acute toxicity testing on freshwater invertebrates because mancozeb is toxic to aquatic invertebrates, binds to sediment, and may persist on sediment surfaces. EFED is uncertain about the risk to benthic organisms.

Endocrine Disruption

Mancozeb toxicity effects noted in both birds and mammals could be a result of hormonal disruptions. The observed effects would support the concern that mancozeb may be an endocrine disruptor. The avian reproductive studies reviewed by EFED noted reproductive effects such as the delay in the onset of egg production, reductions in the hatchlings' and 14-day old survivors' weights, and the reduction in the number of 14-day old survivors. For mammals, EFED noted chronic effects in a 3-month feeding study using rats. Effects noted in females rats included decreased serum thyroxine levels. Male rat effects included: body weight decrements; changes in thyroid hormones; changes in liver enzymes; microscopic changes in the liver and thyroids; increased absolute and relative thyroid weights; and increased relative liver weights. Some developmental effects noted in

mammals (that is, rats) were gross developmental defects, central nervous system defects, skeletal defects, cryptorchidism (failure of one or more testes to descend into the scrotum), and abortions. Chronic testing in freshwater organisms showed immobility, length and time until first brood in daphnia and reduced survival and lack of growth effects in fathead minnow. These effects noted in freshwater species could be a result of hormonal disruptions and would suggest that mancozeb may be an endocrine disruptor.

Data Gaps

Environmental Fate

Comparison data are required concerning particle size and molecular weight distribution for parent mancozeb used in the studies with that present in formulated products due to known effects of such characteristics on hydrolytic stability. In addition to particle size distribution, full characterization of the processes involved in *mancozeb parent* dissipation requires additional information on:

- (1) Coordination geometry and strength between Mn^{+2} and Zn^{+2} ions and sulfur in the EBDC ligand. Data such as vibrational spectroscopy data (Raman; Infrared) are needed to help elucidate the structure of mancozeb. Available structural data are inadequate for determining the strength of the metal-to-sulfur bond.
- (2) Effects of mancozeb particle size, aqueous media pH and concentrations of O_2 and metal ions (i.e. Na, K) on the rate/nature of decomposition of polymeric metiram.
- (3) The release of Mn and Zn ions from mancozeb in order to evaluate possible environmental risk that might be associated with such release in specific environmental settings.

Complete characterization of the fate of *mancozeb residue* requires more information on the various species that constitute this residue including the soil/sediment *bound species*. Information needed are for each of these constituents and includes: their physicochemical properties and the nature of their association with soil/sediment particles.

Several problems were identified in submitted fate studies for the EBDCs including metiram. These problems are presented in details in Appendix I. The registrant is requested to address these problems. The following Table lists the status of the fate data requirements for mancozeb.

Status of environmental fate data requirements for Mancozeb.

Guideline		Data Requirement	Is Data Requirement Satisfied?	MRID Number	Study Classification
161-1	835.2	Hydrolysis ¹	Partially	000971-62 with 402582-01	Supplemental
161-2	835.2	Photo Degradation in Water ²	Yes	001621-03	Acceptable
161-3	835.2	Photo Degradation on Soil ²	Yes	002639-07	Acceptable

162-1	835.4	Aerobic Soil Metabolism ³	Partially	001621-05 with 408387-01	Supplemental		
				457445-01			
162-2	835.4	Anaerobic Soil	No	411771-01 and part of 001621-05	Not Acceptable		
162-3	835.4	Anaerobic Aquatic Metabolism	Partially	000888-20 with 402582-03	Supplemental		
162-4	835.4	Aerobic Aquatic Metabolism	?	459069-01?	? .		
163-1	835.1230	Adsorption/Desorption ⁴		000888-22			
			Partially	402229-01	Supplemental		
	835.1240	Leaching 5	Partially	405883-02	Supplemental		
164-1	835.6	Terrestrial Field Dissipation ⁶	No	409236-01 with 445241-01	Upgradable		
202-1	840.1	Drift Field Evaluation	Reserved (Spray Drift Task Force?)				
201-1	840.1	Droplet Size Spectrum	Reserved (Spray Drift Task Force?)				
165-4	850.2	Accumulation in Fish	ccumulation in Fish Waived because mancozeb K _{ow} is equal to				

The hydrolysis study was first submitted under MRID 00088-19 and under MRID 402582-02 (A better copy but without the 4 appendices attached). The same study was also submitted under MRIDs 000889-16 and 00649-26. MRIDs 00971-55 and 00971-59 are a non-guideline studies. MRID 403819-30 is only a 4 hour study dealing with changes in the tank mix of suspended mancozeb in tap water. It indicated a slight increase in ETU over what was present in the formulation used (Manufacturing process).

² Water and soil photolysis studies was submitted also for DCI under MRIDs 002639-07 and 002588-96.

Ecotoxicity

EFED is uncertain about mancozeb's acute risk to aquatic and terrestrial plants because EFED lacks toxicity data for some or all surrogate species representing these groups. Because EFED lacks chronic mancozeb toxicity data, EFED is uncertain about the chronic risks to estuarine/marine organisms. EFED needs studies presented to evaluate these uncertainties. EFED needs whole sediment acute toxicity testing on freshwater invertebrates because mancozeb is toxic to aquatic invertebrates, binds to sediment, and may persist on sediment surfaces. In some risk evaluations EFED has used supplemental studies to make a risk determination. EFED needs core studies to confirm these findings.

³ Study 451542-01 was rejected.

⁴ Study 000888-22 is the same study under MRIDs 001463-70 and 000971-57

⁵ Study 000655-31 was rejected; MRID 000971-54 is a non-guideline simulated run-off study (Note).

⁶ Study 0001481-26 was rejected. Studies 449962-01; 439172-39/38 and 439703-04 are for dimethomorph. A TFD study on six French soils and an article from J. of Pest Management are available. Also a simulation of the environmental fate of Mancozeb/ETU under condition of use (Models CREAMS and GLEAMS) under MRID 418419-01. Other submitted short studies (Notes) include: MRID 014811-26; 001619-35

The following Table lists the status of the ecological data requirements for mancozeb.

Status of environmental ecological data needs for Mancozeb.

Date: May 25, 2004 Case No: 0643 Chemical No: 014504	MANCOZEB DATA NEEDS FOR THE ENVIRONMENTAL FATE AND EFFECTS DIVISION					
Data Requirements	Composition ¹	Use Pattern²	Does EPA Have Data To Satisfy This Need? (Yes, No, Partially)	Bibliographic Citation	Study Classification	Additional Data Needed Under FIFRA 3(c)(2)(B)?
§158.490 WILDLIFE AND	AQUATIC ORGA	ANISMS				
71-1(a) Acute Avian Oral, Quail/Duck	TGAI	1, 2, 3, 4, 10, & 11	Partially	00080716	Supplemental	Yes
71-1(b) Acute Avian Oral, Quail/Duck	(TEP)	1, 2, 3, 4, 10, & 11	No	not applicable	not applicable	No
71-2(a) Acute Avian Diet, Quail	TGAI	1, 2, 3, 4, 10, & 11	No	not applicable	not applicable	Waived ³
71-2(b) Acute Avian Diet, Duck	TGAI	1, 2, 3, 4, 10, & 11	No	not applicable	not applicable	Waived ³
71-3 Wild Mammal Toxicity		1, 2, 3, 4, 10, & 11	No	not applicable	not applicable	No
71-4(a) Avian Reproduction Quail	TGAI	1, 2, 3, 4, 10, & 11	Yes	44159501 44238001	Core Core	No
71-4(b) Avian Reproduction Duck	TGAI	1, 2, 3, 4, 10, & 11	Yes	41948401	Core	No
71-5(a) Simulated Terrestrial Field Study		1, 2, 3, 4, 10, & 11	No	not applicable	not applicable	No
71-5(b) Actual Terrestrial Field Study		1, 2, 3, 4, 10, & 11	No	not applicable	not applicable	No
72-1(a) Acute Fish Toxicity Bluegill	TGAI	1, 2, 3, 4, 10, & 11	Yes	40118501 00097173 00097147 not reported	Supplemental Supplemental Supplemental Supplemental	Yes
72-1(b) Acute Fish Toxicity Bluegill	(TEP)	1, 2, 3, 4, 10, & 11	No	not applicable	not applicable	Reserved ⁴
72-1(c) Acute Fish Toxicity Rainbow Trout	TGAI	1, 2, 3, 4, 10, & 11	Yes	40118502 not reported	Core Supplemental	No
72-1(d) Acute Fish Toxicity Rainbow Trout	(TEP)	1, 2, 3, 4, 10, & 11	Partially	40467501 43917218 43917216 43917217	Supplemental Supplemental Supplemental Supplemental	Reserved⁴
72-2(a) Acute Aquatic Invertebrate Toxicity	TGAI	1, 2, 3, 4, 10, & 11	Yes	40118503 40467503	Core Core	No
72-2(b) Acute Aquatic Invertebrate Toxicity	(TEP)	1, 2, 3, 4, 10, & 11	Partially	43917217 43917216 43917215	Supplemental Supplemental Supplemental	Reserved ⁴
72-3(a) Acute Estu/Mari Tox Fish	TGAI	1, 2, 3, 4, 10, & 11	No	40586802 41844901	Supplemental Supplemental	Yes

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MANCOZEB DATA NEEDS FOR THE ENVIRONMENTAL FATE AND EFFECTS DIVISION

Data Requirements	Composition ¹	Use Pattern ²	Does EPA Have Data To Satisfy This Need? (Yes, No, Partially)	Bibliographic Citation	Study Classification	Additional Data Needed Under FIFRA 3(c)(2)(B)?
72-3(b) Acute Estu/Mari Tox Mollusk	TGAI	1, 2, 3, 4, 10, & 11	Yes	40885102	Core	No
72-3(c) Acute Estu Mari Tox Shrimp	TGAI	1, 2, 3, 4, 10, & 11	No	41822901 40586801	Supplemental Supplemental	Yes ⁵
850.1740 Whole Sediment Acute Toxicity Invertebrates, Est/Mar	TGAI	1, 2, 3, 4, 10, & 11	No	Not applicable	Not applicable	Yes
72-3(d) Acute Estu/Mari Tox Fish	(TEP)	1, 2, 3, 4, 10, & 11	No	41844902 40586804	Supplemental Supplemental	Reserved ⁴
72-3(e) Acute Estu/Mari Tox Mollusk	(TEP)	1, 2, 3, 4, 10, & 11	Partially	40885101	Core	Reserved ⁴
72-3(f) Acute Estu/Mari Tox Shrimp	(TEP)	1, 2, 3, 4, 10, & 11	No	41822902 40586803	Supplemental Supplemental	Yes
72-4(a) Early Life-Stage Fish	TGAI	1, 2, 3, 4, 10, & 11	Partially	43230701 (freshwater)	Core	Yes ⁶
72-4(b) Life-Cycle Aquatic Invertebrate	TGAI	1, 2, 3, 4, 10, & 11	Partially	40953802 (freshwater)	Core	Yes ⁷
72-5 Life-Cycle Fish (Freshwater Fish)	TGAI	1, 2, 3, 4, 10, & 11	No	Not applicable	Not applicable	Yes
72-6 Aquatic Org. Accumulation	TGAI	1, 2, 3, 4, 10, & 11		•		
72-7(a) Simulated Aquatic Field Study	(TEP)	1, 2, 3, 4, 10, & 11	Not applicable (not required)	44944401	Supplemental9	No
72-7(b) Actual Aquatic Field Study		1, 2, 3, 4, 10, & 11	No	Not applicable	Not applicable	No
§158.540 PLANT PROTE	CTION					
122-1(a) Seed Germ./Seedling Emerg Tier I	(TEP)	1, 2, 3, 4, 10, & 11	Partially	44283401	Core	Yes ¹⁰
122-1(b) Vegetative Vigor-Tier I	(TEP)	1, 2, 3, 4, 10, & 11	Partially	44283401	Core	Yes ¹⁰
122-2 Aquatic Plant Growth-Tier I	(TEP)	1, 2, 3, 4, 10, & 11	No	Not applicable	Not applicable	Yes ⁸
123-1(a) Seed Germ./Seedling Emerg Tier II	(TEP)	1, 2, 3, 4, 10, & 11	No	Not applicable	Not applicable	Reserved
123-1(b) Vegetative Vigor-Tier II	(TEP)	1, 2, 3, 4, 10, & 11	No	Not applicable	Not applicable	Reserved
123-2 Aquatic Plant Growth-Tier II	(TEP)	1, 2, 3, 4, 10, & 11	Partially	43664701 44283402 43917217	Core Core Supplemental	Yes ⁸
124-1 Terrestrial Field Study		1, 2, 3, 4, 10, & 11	No	Not applicable	Not applicable	No

Date: May 25, 2004 Case No: 0643 Chemical No: 014504

MANCOZEB DATA NEEDS FOR THE ENVIRONMENTAL FATE AND EFFECTS DIVISION

Data Requirements	Composition ¹	Use Pattern²	Does EPA Have Data To Satisfy This Need? (Yes, No, Partially)	Bibliographic Citation	Study Classification	Additional Data Needed Under FIFRA 3(c)(2)(B)?
124-2 Aquatic Field Study		1, 2, 3, 4, 10, & 11	No	Not applicable	Not applicable	No
§158.490 INSECT TESTI	NG					
141-1 Honey Bee Acute Contact	TGAI	1, 2, 3, 4, 10, & 11	Yes	00018842	Core	No
141-2 Honey Bee Residue on Foliage	(TEP)	1, 2, 3, 4, 10, & 11	No	00001949	Supplemental	No
141-5 Field Test for Pollinators		1, 2, 3, 4, 10, & 11	No	not applicable	not applicable	No

- 1. Composition: product
- $TGAI = Technical \ grade \ of the \ active \ ingredient; \ PAIRA = Pure \ active \ ingredient, \ radiolabeled; \ TEP = Typical \ end-use$
- 2. Use Patterns:
- 1=Terrestrial/Food; 2=Terrestrial/Feed; 3=Terrestrial Non-Food; 4=Aquatic Food; 5=Aquatic Non-Food (Outdoor); 6=Aquatic Non-Food (Industrial); 7=Aquatic Non-Food (Residential); 8=Greenhouse Food; 9=Greenhouse Non-Food; 10=Forestry; 11=Residential Outdoor; 12=Indoor Food; 13=Indoor Non-Food; 14=Indoor Medical; 15=Indoor Residential
- 3. Waived for mancozeb per memorandum, dated 10/87, from EFED to RD.
- 4. Additional studies on multible active ingredient (MAI) mancozeb TEPs may be required in the future if these TEPs are identified as being of toxicological concern. MRID No. 40467501 has been downgraded from Core to Supplemental because the endpoint results were not based on measure concentrations of the test substance.
- 5. Core study for TGAI of mancozeb is required.
- 6. Core study for estuarine/marine fish for the TGAI of mancozeb is required.
- 7. Core study for estuarine/marine invertebrate for the TGAI of mancozeb is required.
- 8. Tier I or Tier II aquatic plant growth testing needs to be submitted for duckweed (*Lemna gibba*), marine diatom (*Skeletonema costatum*), blue-green algae (*Anabaena flos-aquae*), and a freshwater diatom for mancozeb.
- 9. Mesocosm draft study given abbreviated review with final submitted under MRID No. 45014901 to be reviewed. This submission was not an EFED data requirement but was submitted under section 6 (a)(2) of FIFRA.
- 10. SAI TEP testing is recommended for mancozeb.

Environmental Hazards Labeling Statements for Mancozeb

Manufacturing Use

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries oceans or other waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System (NPDES) permit and the permitting authority has been notified in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance contact your State Water Board or Regional Office of the EPA.

End Use Products

Do not apply directly to water or to areas where surface water is present or to intertidal areas below the mean high-water mark. Do not contaminate water when disposing of equipment wash water or rinsate.

Label statements for spray drift management

AVOIDING SPRAY DRIFT AT THE APPLICATION SITE IS THE RESPONSIBILITY OF THE APPLICATOR. The interaction of many equipment-and-weather-related factors determine the potential for spray drift. The applicator is responsible for considering all these factors when making decisions. Where states have more stringent regulations, they should be observed.